

CHAPTER VI
**DOUBLE COATING VIA REPEAT ADMICELLAR POLYMERIZATION FOR
PREPARATION OF TWO-FUNCTIONAL COTTON FABRIC: ULTRAVIOLET
PROTECTION AND WATER REPELLENCE**

6.1 Abstract

Two-functional cotton fabric was produced by double coating via repeat admicellar polymerization using dodecylbenzenesulfonic acid, sodium salt (DBSA) as the surfactant. 2-Hydroxy-4-acryloyloxybenzophenone (HAB) was first coated on a cotton fabric in order to improve its ultraviolet protection and then methacryloxymethyltrimethylsilane (MSi) was coated to create a hydrophobic surface. Adsorption of DBSA on the HAB-coated substrate was found to be less than on the untreated surface. The polymeric coating on the surface was characterized by SEM and FTIR and found that the double coating process was successful. The treated fabric was found to have very good Ultraviolet Protection Factor (UPF) together with high water repellency as determined by the contact angle measurement. The optimum amount of monomers was found to be 1.5 mM HAB and 10 mM MSi.

Key words: Admicellar polymerization; Cotton fabric; UV Protection; Water repellency

6.2 Introduction

Demands for comfort and healthy lifestyles make it desirable to have textile products with multifunctionality. Moreover, such products can also be the answers for some special applications with enhanced commercial value. Incorporated properties for textiles such as durability, self-cleaning, flame retardancy, antimicrobial and thermochromic characteristics, all have potential industrial applications. Thus, there has been an increase in the study of multifunctional textiles such as hydrophilic or substrate-

independent dyeing and antimicrobial fabrics,¹ water-repellent and antibacterial nylon fabrics,² antimicrobial and blood repellent cotton and nonwoven fabrics,³ UV-resistant and water-repellent fabrics,⁴ water and oil-repellent and flame-retardant wool,⁵ and oil-repellent and shrink-resistant wool.⁶ In many cases various methods of fiber surface modifications were used to impart the required properties to the fabric.

Admicellar polymerization is a versatile method for forming ultrathin polymeric film on a substrate surface.^{7,8} It consists of 3 main steps. Firstly, an admicelle, a surfactant bilayer, is formed on the substrate surface. Secondly, an organic monomer is added into the system, and due to its hydrophobicity, it will preferentially diffuse into the hydrophobic core of the admicelle in a process called adsolubilization. Thirdly, polymerization of the monomer in the admicelle is initiated through the addition of a suitable initiator. After the completion of the reaction, weakly bound surfactant is washed away, leaving a thin polymer film coating on the surface. This method has been used to form a polymer film on various substrates such as alumina,⁹ calcium carbonate,¹⁰ glass fiber,¹¹ mica¹² and cellulose.¹³ More recently, the method has been used on textile materials to produce water repellent cotton,¹⁴ low-resistivity fabric¹⁵ and hydrophilic polyester fabrics,¹⁶ antimicrobial cotton,¹⁷ UV-protective cotton,¹⁸ and self-extinguishing cotton.¹⁹ Compared to pad-dry-cure, the conventional method for applying finishing agents to fabrics, admicellar polymerization offers a number of advantages. It is simple with low energy consumption, water-based and can be carried out using the conventional exhaust dyeing machines. In addition admicellar polymerization has been shown to produce ultrathin film in nanoscale,¹² hence the fabric also retains its pliability and soft touch. Methachan *et al.*²⁰ showed that admicellar-treated fabric also retains its good air permeability indicating that there was no blocking of the interstices between fibers and yarns in the fabric structure. However, there has been no report on preparing a multifunctional textile using admicellar polymerization. Since the film formed by this technique is very thin, it becomes possible to be double coated and combined functionality can be achieved.

In this work admicellar polymerization was used to produce a bifunctional cotton fabric possessing both UV-protective and water-repellent properties. Such fabrics will be suitable for outdoor usage where both UV-protection and water repellency are required such as covering materials and protective clothing. For UV-protective properties, a monomer with UV absorber shown in Figure 6.1. 2-Hydroxy-4-acryloyloxy-benzophenone (HAB) was used as it provides excellent UV-protection as previously reported.²¹ For water-repellency, most studies are based on treating textiles with fluorinated²²⁻²⁴ and silicon compounds.²⁵⁻²⁷ Although fluorochemicals have very low surface energy, they have high cost and pose potential risk to humans and the environment. In this study a silicon compound, methacryloxymethyltrimethylsilane (MSi), was chosen as the monomer to form a hydrophobic surface since tetramethylsilane, a similar compound, was successfully used for hydrophobic coating.²⁸ The double-coating fabrics were characterized using SEM and FTIR and their UV-protection property and water-repellency were determined.

6.3 Experimental

6.3.1 Materials

A plain weave, medium-weight (150 g/m²) cotton fabric was purchased from Boonchaury Co. Ltd. (Thailand) The fabric was desized, scoured, and bleached at the factory. Prior to use, the fabric was washed in a washing machine at 95°C several times until it was free from any remaining surfactant.

Dodecylbenzenesulfonic acid, sodium salt (DBSA) and azobisisobutyronitrile (AIBN) (99%) were purchased from Aldrich Company (USA). Methacryloxymethyltrimethylsilane (MSi) (>95%) was purchased from Gelest Inc., (USA). Ammonium persulfate (99%) was purchased from Asia Pacific Specialty Chemicals Ltd (Australia). Dimethylacetamide (99.5%), ethanol (99%) and sodium chloride (99%) were purchased from Labscan Company (Ireland). All chemicals were used without further purification. 2-Hydroxy-4-acryloyloxybenzophenone (HAB) was

synthesized from acryloylchloride and 2,4-dihydroxybenzophenone. Details of materials, synthesis method, and identification of the product were described elsewhere.²¹

6.3.2 Adsorption isotherm

Adsorption isotherms of the DBSA on untreated and HAB-treated cotton were obtained by exposing a 6.5 cm × 6.5 cm cotton fabric to 35 mL of DBSA solution of known initial concentration. The pH of the solution was pre-adjusted to 4 and 0.15 M NaCl was added. The sealed vial was then placed in a water bath at 30 °C and shaken at 120 rpm for 15 h. Concentrations of supernatant were determined by Shimadzu UV spectrophotometer 2550 at 224 nm. The adsorbed DBSA on cotton was calculated by taking the difference between the initial and final concentrations of DBSA in the vial. The initial DBSA concentration in this experiment was varied to cover the regions below and above the CMC of DBSA.

6.3.3 Admicellar polymerization

Polymerization of HAB on cotton was carried out as in previous work.²¹ A 6.5 × 6.5 cm² cotton fabric was placed in a 40-mL vial containing 0.6 mM DBSA solution with 0.15 M NaCl at pH 4. HAB of 1.5 mM was added into the solution to allow surfactant adsorption and monomer adsolubilization to occur simultaneously at the temperature of 70°C for 6 h. Dimethylacetamide was used as a solvent for HAB and the volume of the organic solvent was kept at 2.5 mL in a total volume of 35 mL. Then 1 mL aqueous ammonium persulfate solution was injected to give an initiator:monomer molar ratio of 1:2. After 15 h of polymerization, the fabric was taken out from the vial and washed with 70°C water for three times to remove the surfactant. The fabric was finally placed in an oven at 60°C until dry.

Polymerization of MSi on an untreated cotton fabric and on the HAB treated cotton was carried out in a vial containing a 6.5 × 6.5 cm² cotton fabric and 0.6 mM DBSA solution with 0.15 M NaCl at pH 4. MSi and AIBN in ethanol with the desired concentrations were added into the aqueous solution and the volume of ethanol

was kept at 10%. An initiator:monomer molar ratio was kept at 1:2. The sealed vial was then placed in a water bath at 30°C and shaken at 120 rpm for 24 h to allow surfactant adsorption and monomer adsolubilization to occur simultaneously. The temperature was then raised to 70°C to initiate the polymerization reaction. After 15 h of polymerization, the fabric was taken out from the vial and washed with 70°C water for three times to remove the surfactant. The fabric was dried in an oven at 60°C.

6.3.4 Characterization of the polymer coating on cotton surface

Scanning electron microscopy (SEM) (JEOL, JSM 5200, 15 kv) was used to study surface morphology of the coated fabric. Fourier transform infrared attenuated total reflectance spectroscopy (FTIR-ATR) with a ZnSe plate was used to analyze the chemical groups present in the polymer coating. The spectrometer used was Nexus 670 spectrometer (Nicolet) with 50 scans at a 4 cm^{-1} resolution in the wavenumber range of $4000 - 650\text{ cm}^{-1}$.

6.3.5 Determination of the contact angle and UV-protective property of the treated fabric

The water contact angle of the treated surface was measured using a KRÜSS contact angle measurement instrument, DSA 10-Mk2. A water droplet with the volume of $10\text{ }\mu\text{L}$ was placed onto the tested surface and its contact angles were measured at 0 and 5 min. Five measurements were carried out on a sample at 5 different positions and the average value was reported.

The UV-protective property of the fabric was determined according to AATCC Test Method 183-2004.²⁹ The UV transmittance of the fabric was measured using a Shimadzu UV spectrophotometer 2550 with integrating sphere attachment ISR-2200. The percent transmittance for wavelengths from 280 to 400 nm was measured in intervals of 2 nm. Three measurements of the UV transmittance were performed for each

specimen, in warp, weft and 45° directions. The results are the mean values of the three measurements of each duplicate specimen.

6.4 Results and Discussion

6.4.1 Surfactant adsorption

Adsorption of DBSA on untreated cotton and HAB-coated cotton were studied and compared. From the isotherm, the DBSA concentration of 0.6 mM which was just below the critical micelle concentration (CMC) of the surfactant solution was chosen for use in the admicellar polymerization process in order to avoid an emulsion polymerization. In Figure 6.2 the amount of DBSA adsorption at plateau region was 14.5 $\mu\text{mol/g}$ cotton. This compares to an equilibrium adsorption of DBSA on the untreated cotton of 20.7 $\mu\text{mol/g}$ cotton under the same condition. With just one hydroxyl group per molecule, cotton fabric coated with poly(HAB) can be expected to be less hydrophilic than untreated cotton. Thus, the amount of the DBSA adsorption on the HAB-treated cotton was lower than the adsorption on the untreated cotton. Based on this result, the double coating process was proposed and shown schematically in Figure 6.3.

6.4.2 Characterization of polymer coating on cotton fabrics

The presence of poly(HAB) on the cotton surface after admicellar polymerization was confirmed by SEM and FTIR. SEM micrograph in Figure 6.4 (a) shows the clean surface of untreated cotton fiber. Figure 6.4 (b)-(f) show that the polymer was successfully coated on the fiber surface. The cotton surface treated by MSi of 5 mM and 10 mM were shown as Figure 6.4 (b) and (c) respectively. The film of poly(MSi) in Figure 6.4 (b) becomes smoother as the concentration of MSi increases in Figure 6.4 (c). The poly(HAB)-coated surface in Figure 6.4 (d) shows that the polymer was uniformly coated on the fiber surface as well. The polymer on the surface appears as a rough film since it comes from many reaction sites at which polymerization initiated and spread over the substrate. The surface area of cotton was found to be 4 m^2/g determined from BET with nitrogen.¹⁴ A thickness of polymer film was estimated

assuming 100% conversion of MSi to polymer and a density of 1 g/cm^3 . Assuming that the film is evenly distributed over the surface and that all the surface area from BET is accessible, the thickness of poly(HAB) at the HAB amount of 1.5 mM was found to be 2.8 nm. The thickness of poly(MSi) at the MSi amounts of 5 and 10 mM was 5.9 and 11.8 nm, respectively. These thickness values agree with the previous work that a polymer film forming by admicellar polymerization is ultrathin in nanoscale.¹² After the second coating by 5 mM MSi onto the poly(HAB)-coated surface, the surface morphology changes from the connected-nanoparticle like film to surface features larger in size, appearing smoother locally and more integrated (Figure 6.4 (e)). When the concentration of MSi increases, the scale of surface features increases further and some sites where the polymer grows well can be observed as shown in Figure 6.4 (f). This swelling of polymer on the surface may result from the monomer MSi absorbing into poly(MSi) as the reaction proceeds. Wu found evidence for this in admicellar polymerization of styrene.⁸ The cotton fiber treated by 1.5 mM HAB/10 mM MSi does not show a very smooth surface as that of the fiber treated by 10 mM MSi only. This may be due to the fact that the second adsorption of DBSA on the HAB-treated cotton was not as uniform as the adsorption on the untreated cotton. Comparing Fig 4 (d) and (e), it can be seen that there was a distinctive change in the surface morphology after MSi was coated onto the HAB-coated surface, indicating that poly(MSi) was successfully double coated.

Figure 6.5 (b) shows the FTIR spectrum of the HAB-treated cotton compared to the untreated cotton shown in Figure 6.5 (a). The bands at 2900 cm^{-1} and 3300 cm^{-1} were assigned to C-H and O-H bonds which normally appear on cotton surface. The peak at 1760 cm^{-1} is due to C=O stretching of phenolic ester group in HAB unit. The strong band at 1630 cm^{-1} is assigned to C=O of ketone groups. The band in the region of 1245 cm^{-1} is assigned to the C-O stretching of a phenolic ester.³⁰ For the MSi-treated cotton in Figure 6.5 (c), there is the strong band at 1725 cm^{-1} which is due to C=O stretching of aliphatic ester group in MSi unit. The bands at 850 cm^{-1} and 750 cm^{-1} are assigned to Si-CH₃ and Si-C bonds.³¹⁻³² The FTIR spectrum of the HAB/MSi treated

cotton in Figure 6.5 (d) shows characteristic bands of both HAB and MSi, thus confirming that poly(MSi) has been successfully coated to the poly(HAB)-coated surface. The bands of MSi were found to have a higher intensity than that of HAB due to its presence at the outer surface.

6.4.3 UV protection properties of the treated cotton fabrics

According to AATCC Test Method 183-2004,²⁹ Ultraviolet Protection Factor (UPF) is defined as the ratio of the average effective UV irradiance calculated for unprotected skin to the average effective UV irradiance calculated for skin protected by the test fabric. UPF is calculated as follows:

$$UPF = \frac{\sum_{280\text{ nm}}^{400\text{ nm}} E_{\lambda} S_{\lambda} \Delta\lambda}{\sum_{280\text{ nm}}^{400\text{ nm}} E_{\lambda} S_{\lambda} T_{\lambda} \Delta\lambda} \quad (6.1)$$

where:

E_{λ} = relative erythemal spectral effectiveness

S_{λ} = solar spectral irradiance ($\text{Wm}^{-2}\text{nm}^{-1}$)

T_{λ} = average spectral transmittance of fabric

$\Delta\lambda$ = wavelength interval for measurements (nm)

λ = wavelength (nm)

E_{λ} is the erythema action spectrum developed by International Commission on Illumination or CIE.³³ It is a spectral dependence of the ability of UV radiation to produce erythema in human skin. Reference values of E_{λ} and S_{λ} at each wavelength are provided by AATCC Test Method 183-2004.

According to AS/NZS 4399: 1996,³⁴ fabrics can be classified as having an excellent UV protection with a UPF value of 40 and above. The effect of HAB concentration on the UV-protection properties of the admicellar-treated fabric was studied in previous work.²¹ It was found that cotton fabric treated with an HAB concentration higher than 1.2 mM gave excellent UV protection. Thus in this work, an HAB concentration of 1.5 mM HAB was used to prepare the HAB-coated cotton.

Figure 6.6 (a) shows the effect of MSi concentration on UPF of cotton fabrics. When MSi concentration increased, the UPF values of the treated fabrics remained almost unchanged with a UPF value of 4 as untreated cotton. This shows that UPF of the fabric is not affected by MSi as it does not absorb UV light. Similar result was found with double coating as shown in Figure 6.6 (b). The 1.5 mM HAB-treated fabric has an initial UPF value of 48. After the second coating with MSi, the UPF value of the double-coated fabric decreased to around 40 and remained more or less constant for all MSi concentrations. This decrease was attributed to the shielding effect of poly(MSi) on the outermost surface. Thus, even though the efficiency of UV absorption in the double-coated fabric was slightly reduced, the treated fabric still provides excellent UV protection.

6.4.4 Hydrophobicity of the treated cotton fabrics

The hydrophobicity of the cotton fabrics was determined by measurement of water contact angle with the sessile drop method. Contact angles of the cotton fabrics treated by different MSi concentrations appear in Figure 6.7. A water droplet disappears immediately on untreated cotton due to the hydrophilicity of its hydroxyl groups. For MSi-treated cotton, the contact angles at 0 min were all higher than 90° , ranging from 96.7° to 113° which increased with increasing in MSi concentration. There was only a slight decrease in the contact angle after 5 min except from the sample treated with 2 mM MSi where the droplet disappeared at 5 min. The change in the contact angles with time was shown more clearly in Figure 6.8. At 2 mM MSi, the contact angle decreased rapidly to zero within .2 min. At higher MSi concentrations, the contact angles decreased only slightly with time. The water droplet remained more than 30 min on the fabric treated by 10 mM MSi.

Figure 6.9 shows the contact angles of HAB/MSi treated fabric. For the 1.5 mM HAB-treated cotton, the initial contact angle was 83.3° but it decreased rapidly to zero within 10 s. This is due to the interaction n between hydroxyl groups of HAB and

water. When the 1.5 mM HAB-treated cotton was double-coated by MSi, the initial contact angle increased to 104.4° with the use of 2 mM MSi and it rose with increasing in MSi concentration to give the highest observed contact angle of 120° for 10 mM MSi. This is slightly higher than the contact angle of 113° achieved with fabric coated only with MSi at the same MSi concentration. Figure 6.10 shows the change in the contact angle with time up to 5 min. It can be seen that there was much improvement in the fabric treated with 2 mM MSi where the water droplet could stay much longer with a contact angle of 92.8° at 5 min. For higher MSi concentrations, the decrease in the contact angle with time was more gradual.

When the surface energy is lowered, the hydrophobicity is enhanced. Reported values for water contact angles on polypropylene, poly(dimethylsiloxane), and poly(tetrafluoroethylene) are 96°, 102° and 117°.³⁵ However, for wettability surface roughness is the other dominant factor. The effect of surface roughness on wettability has been explained by Wenzel's equation.³⁶

$$\cos \theta_w = r \cos \theta_y \quad (6.2)$$

where θ_w is the apparent contact angle on a rough surface, θ_y is the ideal contact angle on a smooth surface and r is the roughness factor. This equation indicates that the contact angle will increase with increasing roughness of a hydrophobic surface. For this reason, researchers nowadays attempt to introduce roughness to the substrate surface as nanotexture by various methods such as plasma treatment,²⁸ using fumed silica²⁵ and assembly of carbon nanotubes.³⁷ In this work, it can be seen that the contact angle of HAB/MSi-treated fabrics are higher than MSi-treated fabrics for all MSi concentrations. It may be implied that the HAB coating introduces nanotexture or roughness to the cotton surface. As can be seen from SEM results, the poly(HAB) film appears as a rough film on the cotton surface while the poly(MSi) film is smoother. For this reason, the highest contact angle was improved from the value of 113° for the MSi-treated fabric to the value of 120° for the HAB/MSi-treated fabric. The highest contact angle obtained in

this work is close to the contact angle of cotton fabric obtained by hybrid hexadecyltrimethoxysilane-fumed silica coating which was 114-121.6°.²⁵

6.5 Conclusions

HAB polymerization alone does not instill water repellency and MSi polymerization alone fails to provide UV protection. Bifunctional UV-protective and hydrophobic cotton was achieved by double coating via admicellar polymerization of HAB and MSi. The adsorption of a surfactant on a coated surface was found to be less than the adsorption on the untreated cotton. SEM and FTIR results confirmed that the polymer films were coated on the surface. The doubly coated fabric provides an excellent UV protection with a UPF value of around 40 and it has very good water repellency with the highest contact angle of 120°.

6.6 Acknowledgments

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6.7 References

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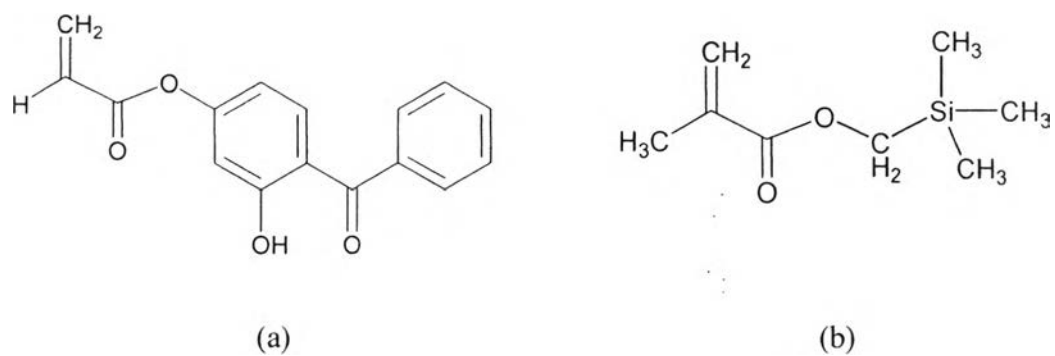


Figure 6.1 Structure of (a) 2-hydroxy-4-acryloyloxybenzophenone (HAB) and (b) Methacryloxymethyltrimethylsilane.

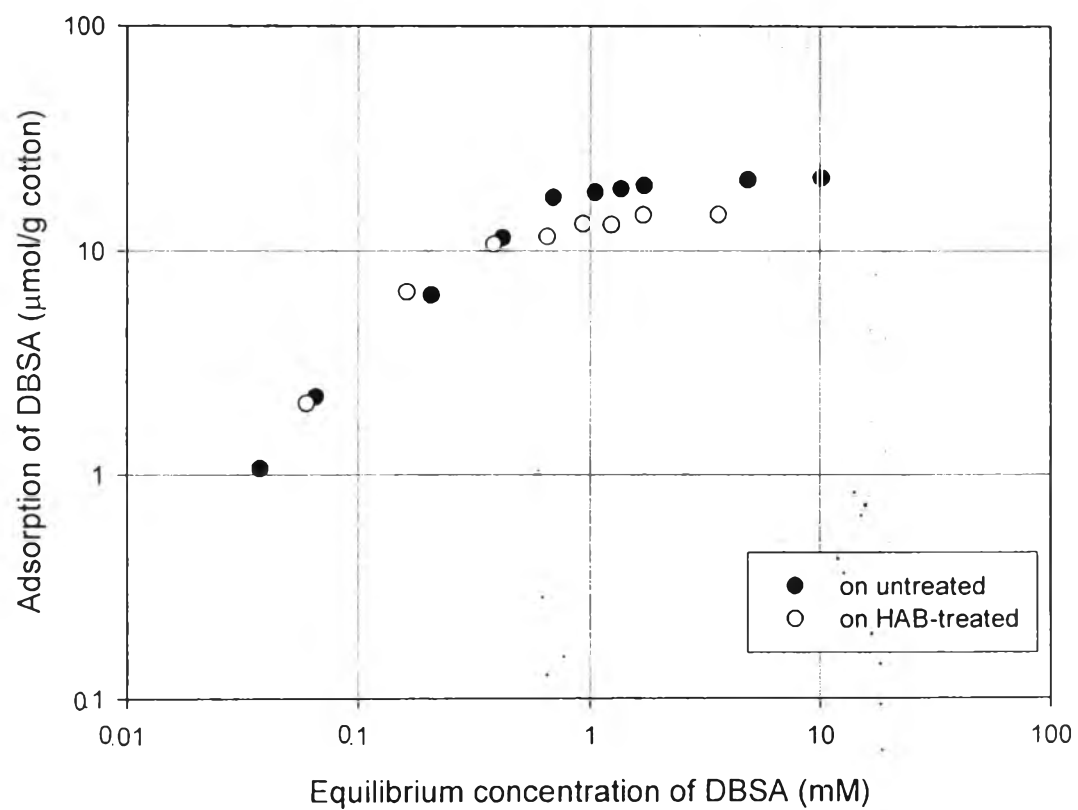


Figure 6.2 Adsorption isotherms of DBSA on cotton untreated and treated by 1.5 mM HAB in the presence of 0.15 M NaCl at 30 °C.

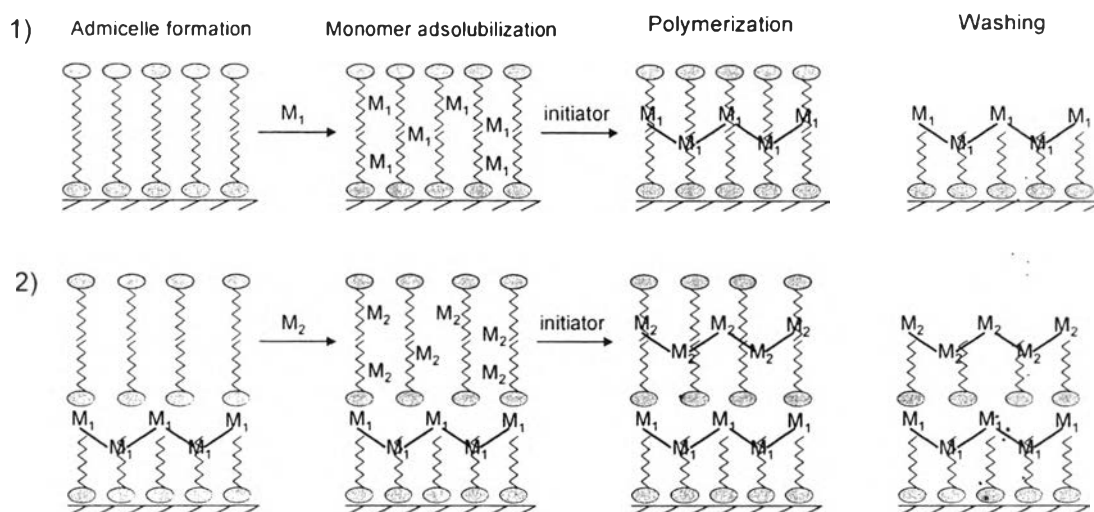


Figure 6.3 Schematic of the proposed double coating process: 1) admicellar polymerization of the first monomer (M_1) on a substrate surface; 2) admicellar polymerization of the second monomer (M_2) on the M_1 -coated surface.

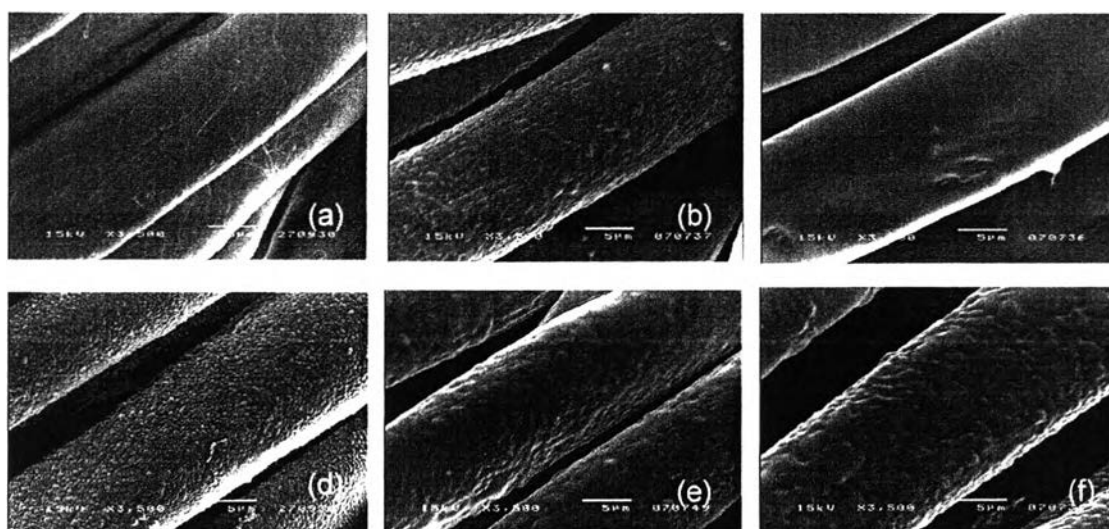


Figure 6.4 SEM micrographs of (a) untreated cotton, and treated-cotton fabrics by using (b) 5 mM MSi, (c) 10 mM MSi, (d) 1.5 mM HAB, (e) 1.5 mM HAB/5 mM MSi and (f) 1.5 mM HAB/10 mM MSi.

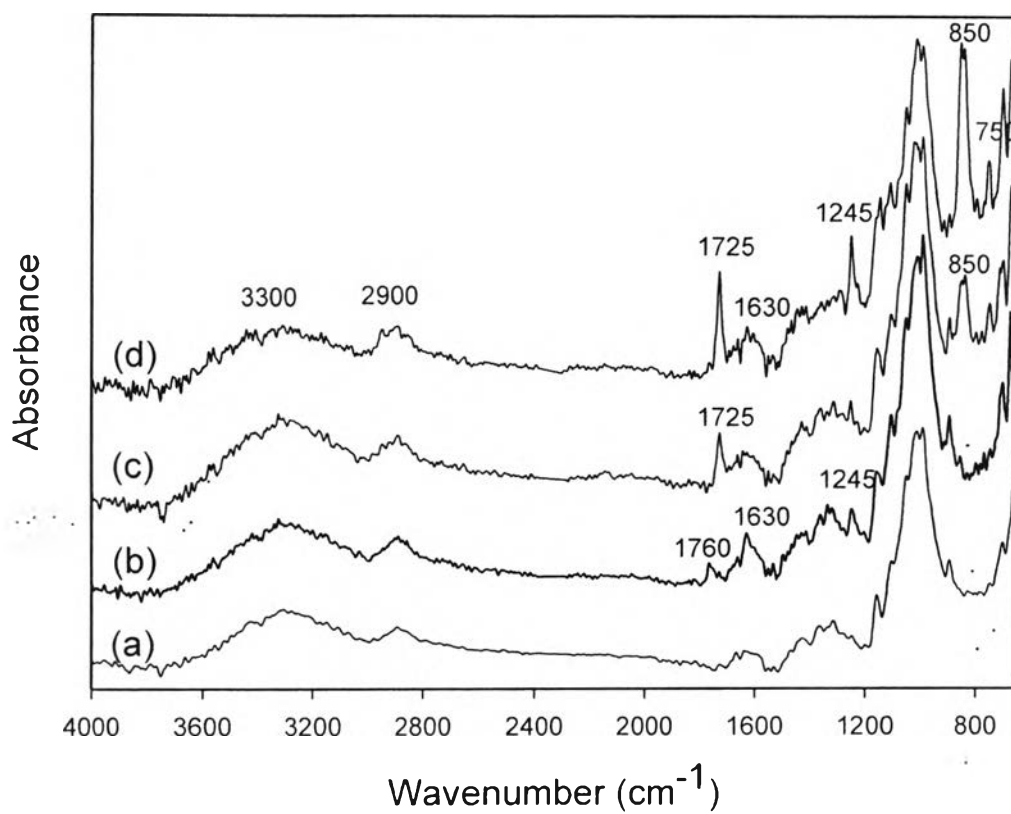


Figure 6.5 The FTIR-ATR spectra of (a) untreated cotton, and treated cotton by using (b) 1.5 mM HAB, (c) 10 mM MSi and (d) 1.5 mM HAB/10 mM MSi.

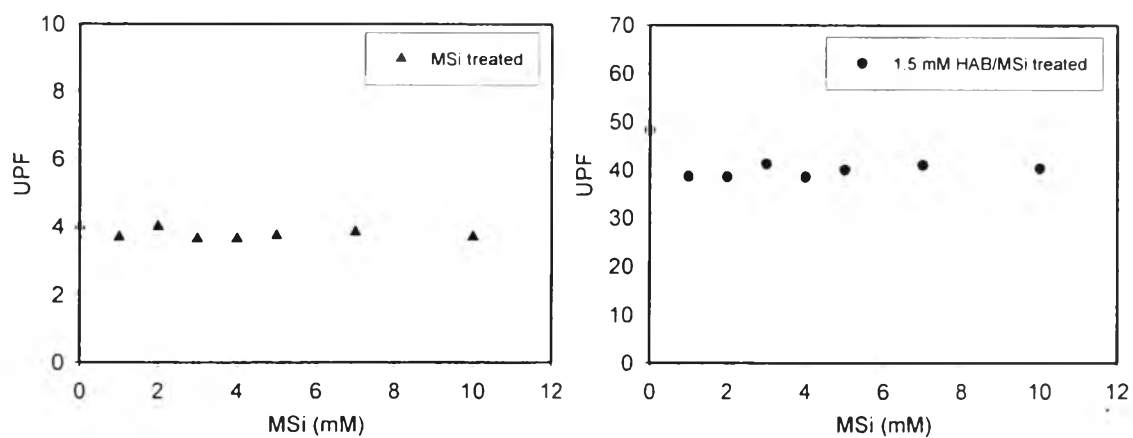


Figure 6.6 UPF of (a) MSi treated cotton fabrics and (b) 1.5 mM HAB/MSi treated fabrics using 0.6 mM DBSA and 0.15 M NaCl.

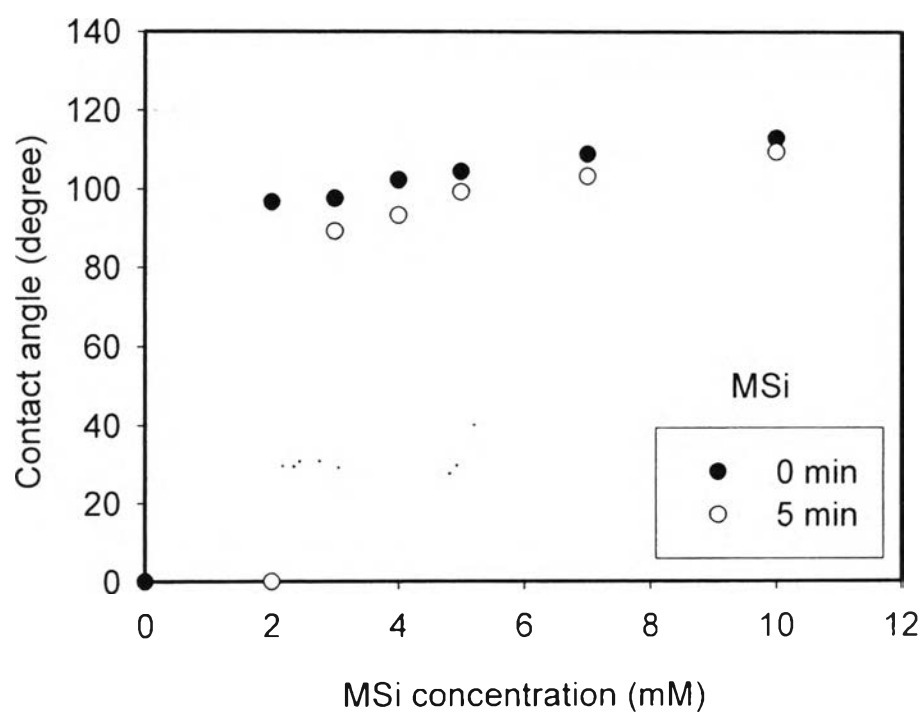


Figure 6.7 Dependence of contact angle on MSi concentration of the MSi-treated cotton fabrics using 0.6 mM DBSA and 0.15 M NaCl.

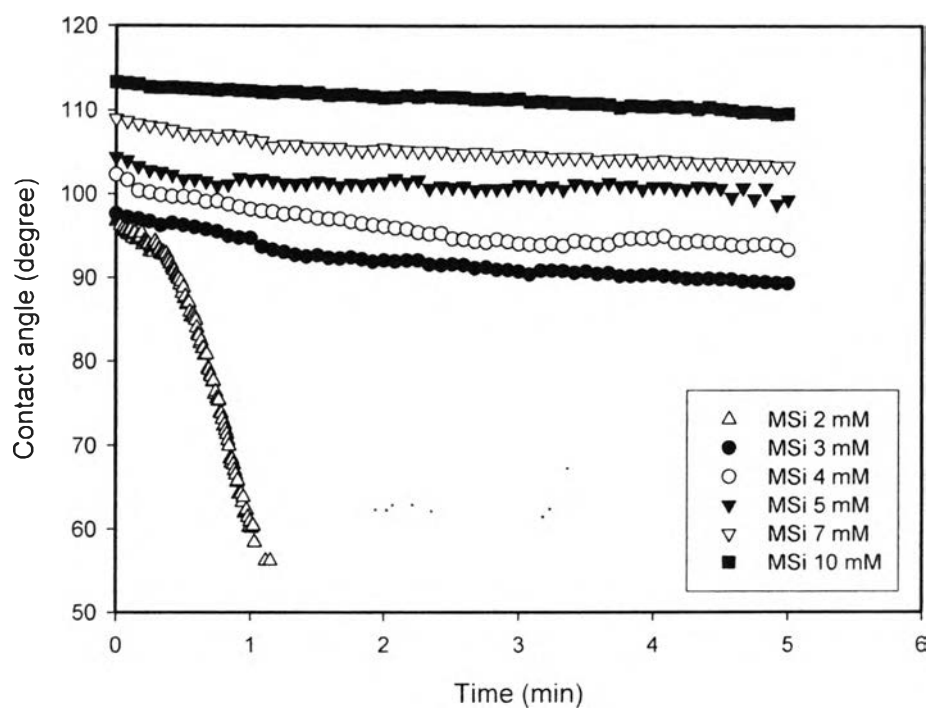


Figure 6.8 Change of contact angles with time of the MSi-treated cotton fabrics using 0.6 mM DBSA, 0.15 M NaCl and different MSi concentrations.

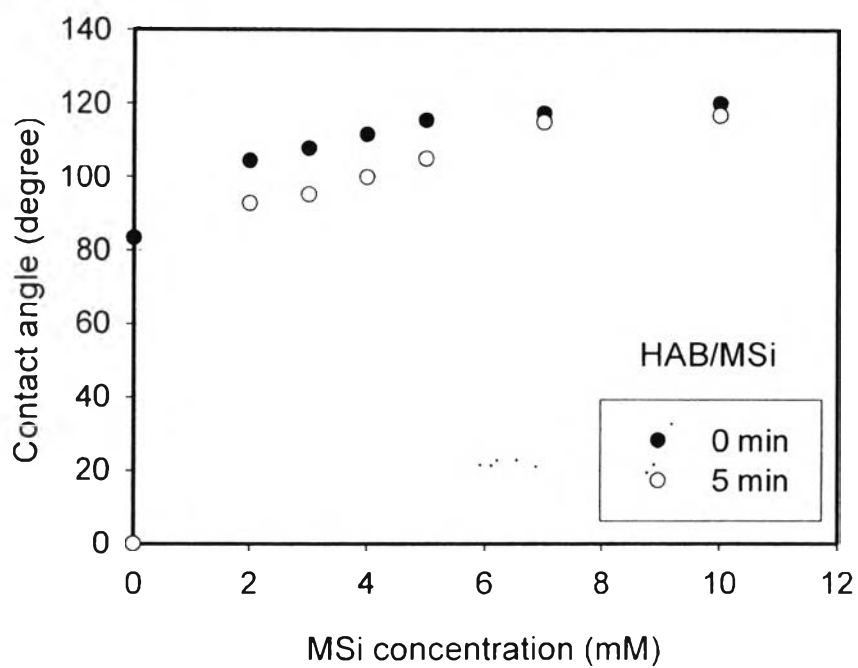


Figure 6.9 Dependence of contact angle on MSi concentration of the HAB/MSi-treated cotton fabrics using 1.5 mM HAB, 0.6 mM DBSA and 0.15 M NaCl.

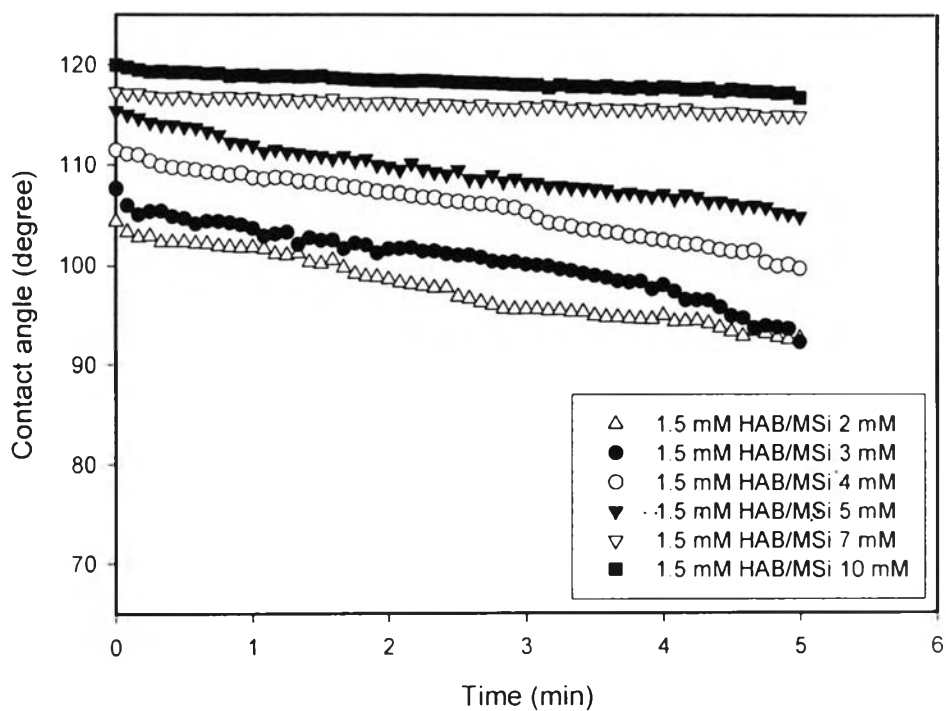


Figure 6.10 Change of contact angles with time of the HAB/MSi-treated cotton fabrics using 1.5 mM HAB, 0.6 mM DBSA, 0.15 M NaCl and different MSi concentrations.